

# Charge and Lattice Dynamics of Ordered State in $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$ : Infrared Reflection Spectroscopy Study

A.P. Litvinchuk<sup>1</sup>, M. N. Iliev<sup>1</sup>, M. Pissas<sup>2</sup>, and C.W. Chu<sup>1,3,4</sup>

<sup>1</sup>*Texas Center for Superconductivity and Advanced Materials,*

*and Department of Physics, University of Houston, Houston, Texas 77204-5002*

<sup>2</sup>*Institute of Material Science, NCSR, Democritos, 153 10 Aghia Paraskevi, Athens, Greece*

<sup>3</sup>*Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720*

<sup>4</sup>*Hong Kong University of Science and Technology, Hong Kong, China*

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We report an infrared reflection spectroscopy study of  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$  over a broad frequency range and temperature interval which covers the transitions from the high temperature paramagnetic to ferromagnetic and, upon further cooling, to antiferromagnetic phase. The structural phase transition, accompanied by a ferromagnetic ordering at  $T_C=234$  K, leads to enrichment of the phonon spectrum. A charge ordered antiferromagnetic insulating ground state develops below the Néel transition temperature  $T_N=163$  K. This is evidenced by the formation of charge density waves and opening of a gap with the magnitude of  $2\Delta_0 = (320 \pm 15) \text{ cm}^{-1}$  in the excitation spectrum. Several of the infrared active phonons are found to exhibit anomalous frequency softening. The experimental data suggest coexistence of ferromagnetic and antiferromagnetic phases at low temperatures.

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Manganite perovskites  $\text{R}_{1-x}\text{A}_x\text{MnO}_3$  (where R is a trivalent rare earth and A is a divalent alkaline rare earth) exhibit rich phase diagram and a variety of intriguing properties due the delicate interplay of spin, charge, lattice, and orbital degrees of freedom (Ref. [1, 2, 3] and references cited therein). Well defined anomalies of physical properties at commensurate carrier concentrations of  $x=N/8$  (where  $N=1, 3, 4, 5$ , and  $7$ ) and  $x = L/3$  (where  $L=1,2$ ) were unambiguously established. Of particular interest is the phenomenon of charge and orbital ordering, most clearly pronounced for  $x=1/2$  [4, 5, 6, 7, 8, 9, 10].

In this communication we report the results of an infrared reflection study of  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$  over broad frequency range and at temperatures, covering the transitions from the high temperature paramagnetic to ferromagnetic and, upon further cooling, to antiferromagnetic phase. By making use of Kramers-Kronig analysis we obtained the spectral dependence of conductivity. Its analysis yields information on the evolution of phonons and electronic excitations as a function of temperature. We found that additional phonon modes appear in the spectra in the ferromagnetic phase, a fact which implies the occurrence of a structural phase transition. Upon further cooling the conductivity spectrum shows development of a gap, which signals the formation of a charge ordered state at low temperatures. At the same time a Drude-like component of the conductivity does not vanish completely and suggests the coexistence of a metallic and insulating phases.

The measurements were performed on a dense ceramic pellet of  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$ , mechanically polished to optical quality. The material preparation technique is described in Ref. [3, 9, 11]. The samples were intensively characterized by the X-ray scattering, neutron diffrac-

tion, magnetization measurements, Raman scattering as well as Mössbauer spectroscopy (doped with 1% Sn or Fe). These measurements unambiguously identified the transition from the paramagnetic to ferromagnetic phase at  $T_C=234$  K, and further to antiferromagnetic phase at  $T_N^c=163$  K (cooling cycle) or  $T_N^h=196$  K (heating cycle), see Fig. 6 in Ref.[3].

The reflection measurements were performed on a Bomem-DA8 Fourier-transform interferometer in the frequency range  $50\text{-}8000 \text{ cm}^{-1}$  with the use of a liquid-helium-cooled bolometer, HgCdTe, and InSb detectors and appropriate beam splitters. Spectral resolution was set to  $1 \text{ cm}^{-1}$ . A gold mirror was used as a reference. The sample was attached to the cold finger of a helium flow cryostat and during measurements the temperature was stabilized to within  $0.2$  K. The reflectance spectra  $R(\omega)$  were extrapolated in the low frequency range by either Hagen-Rubens relation  $(1-R) \sim \omega^{1/2}$  or a constant (at low temperatures) and  $R \sim \omega^{-4}$  for high frequencies up to  $30000 \text{ cm}^{-1}$ . The results of Kramers-Kronig analysis of the spectra show that variation of extrapolated reflection do not influence conductivity values in the frequency range of interest ( $50\text{-}3000 \text{ cm}^{-1}$ ).

The reflectance spectra of  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$  during cooling and heating cycles are shown in Fig. 1 for several temperatures between  $215$  and  $110$  K. As expected, a hysteretic temperature behavior is clearly seen around  $T_N$ , typical for the first-order transition occurring in the CE-type magnetic structure[12]. Indeed, upon cooling the low-frequency reflectance (below  $200 \text{ cm}^{-1}$ ) shows a "metal-like" increase toward lower wavenumbers for the four upper curves on the left panel of Fig. 1, but becomes less frequency dependent for the two lower curves (i.e. below  $145$  K). Instead, during the heating cycle the low-frequency reflectance keeps its behavior from the low

temperatures up to 190 K and becomes more "metal-like" at higher temperatures only.

To obtain more specific information on phonons and the charge dynamics, we performed Kramers-Kronig analysis, which yields the spectral dependence of conductivity. Fig. 2 illustrates the data, obtained in the cooling cycle. The conductivity spectra below  $650\text{ cm}^{-1}$  are dominated by phonons, while at higher frequencies the "background" conductivity steadily increases toward higher wavenumbers with apparent slope becoming larger upon lowering temperature. At  $T=80\text{ K}$  (the lowest panel in Fig. 2) the extrapolation of this background to lower frequencies crosses zero conductivity at positive wavenumbers, i.e. shows zero contribution to the  $dc$  conductivity. It signals opening of a gap, related to the formation of a charge density wave in charge ordered state due to real-space ordering of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions[1, 4, 13].

Theoretical consideration of a charge ordered system yields the following frequency dependence of conductivity[14]:

$$\sigma(\omega) \sim (\omega - 2\Delta)^\alpha, \quad (1)$$

where  $2\Delta$  is the magnitude of the charge gap and  $\alpha = 1/2$ . Using this prediction we fitted the conductivity spectra at frequencies above the highest energy phonon (in the range  $750$  to  $2800\text{ cm}^{-1}$ ) using  $2\Delta$  and  $\alpha$  as parameters. For all temperatures the values of  $\alpha$  are found to be between  $0.51$  and  $0.54$ , in good agreements with the theory. The parameter  $2\Delta$  increases in a linear manner from the negative value of  $-2777\text{ cm}^{-1}$  at room temperature to  $-171\text{ cm}^{-1}$  at  $T=170\text{ K}$  and becomes positive at  $160\text{ K}$  ( $2\Delta = 165\text{ cm}^{-1}$ ), signaling opening of a "real" gap. The temperature, at which this gap opens, unambiguously identifies it as being due to the formation of a charge ordered state in  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$  because the antiferromagnetic transition temperature for the sample is  $T_N^c=163\text{ K}$ . The gap fully opens below  $150\text{ K}$ , where it reaches the value of  $2\Delta_0=(320 \pm 15)\text{ cm}^{-1}$  (Fig. 3).

Earlier experimental study of the charge density waves in  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$  by optical transmission technique yielded the gap value of  $710\text{ cm}^{-1}$  [13]. Even larger value of about  $3600\text{ cm}^{-1}$  was obtained from a reflection studies by Kim et al.[15]. Unlike present measurements, which were performed on a bulk sample, the measurements in Ref. [13] we carried out on pressed pellets of finely milled  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$ , embedded into CsI host matrix. We believe that there are at least two factors, which contributed to an overestimation of  $2\Delta$  in this latter case. First, pellets non-uniformity may introduce scattering of the transmitted light beam and this way increase apparent optical density of the sample. Second, the authors of Ref. [13] performed fitting of the "background" in a very narrow frequency interval  $710\text{--}900\text{ cm}^{-1}$ , which could generate significant error in determining the slope and, correspondingly, the value of  $2\Delta$ . As to the results of Ref. [15], the measurements were performed in a wide frequency range extending up to  $30\text{ eV}$  with emphasis on

the analysis of an intense feature near  $1\text{ eV}$  (due to an interatomic  $\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$  transitions[16]); the authors overlooked evolution of the spectra at lower wavenumbers and lower conductivity values.

Next, we turn to the analysis of phonons, which dominate conductivity at frequencies below  $650\text{ cm}^{-1}$ . The spectra for several temperatures above and below charge ordering temperature  $T_N^c=163\text{ K}$  are shown in Fig. 4. Each spectrum is fitted by a set of Lorentzians, which correspond to phonons. The contribution of free carriers is accounted for by an additional oscillator, centered at zero frequency. As it is seen, with just 5 phonons one can adequately describe the spectrum at  $230\text{ K}$ . At  $215\text{ K}$  two new bands, centered at about  $505$  and  $285\text{ cm}^{-1}$ , appear. Intensity of these bands gradually increases upon lowering temperature down to  $150\text{ K}$ , and then becomes weakly dependent on temperature upon further cooling (Fig. 5(a)). These new lines in the spectra could be a consequence of either the formation of a novel orthorhombic phase below  $T_C=234\text{ K}$ , which has the same symmetry (space group  $Pnma$ ), but slightly different lattice parameters compared to the room temperature phase of  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$ [7], or the appearance of a superstructure with doubled  $a$  lattice parameter and the space group  $P2_1/m$ [5]. The observed intensity increase over rather wide temperature interval below  $T_C$  indicates that the volume fraction of the novel phase increases upon sample cooling, in agreement with[7]. Note that appearance of vibrational modes with very similar frequencies was reported in charge ordered  $(\text{LaPrCa})\text{MnO}_3$  [17].

The number of phonon lines observed in the infrared spectra is small compared to what is predicted by a group theoretical analysis[9, 18]: 25 for the room temperature phase of  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$  (space group  $Pnma$ ) and 63 for the low-temperature charge ordered phase (space group  $P2_1/m$ ). For the parent compound  $\text{LaMnO}_3$ , as shown in the upper panel of Fig. 4, one clearly identifies majority of theoretically predicted lines, as also reported by Paolone et al.[19] and Quijada et al.[20]. The small number of lines observed in  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$  is probably due to the effect of compositional cation disorder ( $\text{La}/\text{Ca}$ ), which considerably shorten the phonon lifetime and, consequently, broaden phonon peaks. Indeed, the typical phonon line width in  $\text{LaMnO}_3$  is  $10\text{--}40\text{ cm}^{-1}$  at room temperature, while it is as high as  $60\text{--}80\text{ cm}^{-1}$  in  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$ . The effect of phonon line broadening is documented in a study of 8% Ca-doped  $\text{LaMnO}_3$ . [19]

Another interesting experimental finding is that several phonon lines exhibit pronounced frequency softening upon entering the charge ordered insulating antiferromagnetic state (Fig. 5 (c,d)). This could be due to the variation of relevant bond distances, documented in the neutron diffraction studies[5, 7] and/or the effect of magnetic order on corresponding force constants, similar to those reported for other magnetic materials[21, 22].

It is important to note that the dielectric response of  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$ , as obtained from the reflection spectroscopy data, is consistent with the phase separation sce-

nario for manganese oxides (see review [23] and references therein). Indeed, even below  $T_N$  the dielectric function is not typical of an insulator, but contains the Drude-like component, a signature for presence in the sample of a conducting phase. Fig. 5(b) shows the temperature dependence of integrated conductivity in the frequency range  $50\text{--}650\text{ cm}^{-1}$  after high-frequency "background" was subtracted. It contains contribution of phonons and low-frequency metallic response. As phonons are only weakly change with temperature (see Fig. 4), this dependence reflects primarily the fraction of conducting (ferromagnetic) phase in the sample: it sharply increases upon entering ferromagnetic state below  $T_C$ , reaches its maximum around  $T_N$ , but does not completely disappear at lower temperatures. This finding is in agreement with earlier reports on  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$  [11, 24, 25, 26, 27]. We have to mention that the presence of a conducting phase has only minor effect on the gap magnitude of the charge ordered state, as determined above. This is due to the fact that the conducting phase affects the dielectric function at low frequencies (below  $300\text{ cm}^{-1}$ ), while the gap magnitude determination involves analysis of the spectra at higher frequencies (above  $750\text{ cm}^{-1}$ ). The different value of the gap compared to that of Ref. [13] could, at least in part, be due to different size of charge ordered domains in the material.

In conclusion, the infrared reflection study of  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$  revealed the occurrence of a structural phase transition at  $T_C$ , evidenced by appearance of additional phonon lines. The charge and orbital ordering below the antiferromagnetic transition temperature  $T_N$  was found to drastically modify the carrier dynamics as charge density waves develop, leading to the creation of a gap in the excitation spectrum with magnitude of  $2\Delta_0 = (320 \pm 15)\text{ cm}^{-1}$ . The experimental data suggest coexistence of ferromagnetic and antiferromagnetic phases at low temperatures.

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- [1] S-W. Cheong and C.H. Chen, in *"Colossal Magnetoresistance, Charge Ordering and Related Properties of Oxide Manganites"*, ed. by C.N.R. Rao and B. Raveau (World Scientific, Singapore, 1998) p.241.
  - [2] J.M.D. Coey, M. Viret, and S. von Molnar, *Adv. Phys.* **48** (1999) 167.
  - [3] M. Pissas and G. Kallias, *Phys. Rev. B* **68** (2003) 134414.
  - [4] C.H. Chen and S-W. Cheong, *Phys. Rev. Lett.* **76** (1996) 4042.
  - [5] P.G. Radaelli, D.E. Cox, M. Marezio, and S-W. Cheong, *Phys. Rev. B* **55** (1997) 3015.
  - [6] S. Mori, C.H. Chen, and S-W. Cheong, *Nature* **392** (1998) 473.
  - [7] Q. Huang, J.W. Lynn, R.W. Erwin, A. Santoro, D.C. Dender, V.N. Smolyaninova, K.G. Ghosh, and R.L. Green, *Phys. Rev. B* **61** (2000) 8895.
  - [8] G. Papavassiliou, M. Fardis, M. Belesi, T.G. Maris, G. Kallias, M. Pissas, and D. Niarchos, *Phys. Rev. Lett.* **84** (2000) 761.
  - [9] M.V. Abrashev, J. Bäckström, L. Börjesson, M. Pissas, N. Kolev, and M.N. Iliev, *Phys. Rev. B* **64** (2001) 144429.
  - [10] S. Naler, M. Rübhausen, S. Yoon, S.L. Cooper, K.H. Kim, and S-W. Cheong, *Phys. Rev. B* **65** (2002) 092401.
  - [11] A. Simopoulos, G. Kallias, E. Devlin, and M. Pissas, *Phys. Rev. B* **63** (2001) 054403.
  - [12] E.O. Wollan and W.C. Koehler, *Phys. Rev.* **100** (1955) 545.
  - [13] P. Calvani, G. De Marzi, P. Dore, P. Masseli, F. D'Amore, S. Sagliardi, and S-W. Cheong, *Phys. Rev. Lett.* **81** (1998) 4504.
  - [14] P.A. Lee, T.M. Rice, and P.W. Anderson, *Solid State Commun.* **14** (1974) 703.
  - [15] K.H. Kim, S. Lee, T.W. Noh, and S-W. Cheong, *Phys. Rev. Lett.* **88** (2002) 167201.
  - [16] J.H. Jung, K.H. Kim, T.W. Noh, E.J. Choi, and J. Yu, *Phys. Rev.* **57** (1998) R11043.
  - [17] H.J. Lee, K.H. Kim, M.W. Kim, T.W. Noh, B.G. Kim, T.Y. Koo, S-W. Cheong, Y.J. Wang, and X. Wei, *Phys. Rev. B* **65** (2002) 115118.
  - [18] I.S. Smirnova, *Physica B* **262** (1999) 247.
  - [19] A. Paolone, P. Roy, A. Pimenov, A. Lloid, O.K. Melnikov, and A.Ya. Shapiro, *Phys. Rev. B* **61** (2000) 11255.
  - [20] M.A. Quijada, J.R. Simpson, L. Vasiliu-Doloc, J.W. Lynn, H.D. Drew, Y.M. Mukovskii, and S.G. Karabashev, *Phys. Rev. B* **64** (2001) 224426.
  - [21] C.C. Homes, M. Ziaei, B.P. Clayman, J.C. Irwin, and J.P. Franck, *Phys. Rev. B* **51** (1995) 3140.
  - [22] A.P. Litvinchuk, M.N. Iliev, V.N. Popov, and M.M. Gospodinov, *J. Phys.: Condens. Matter* **16** (2004) 809.
  - [23] E. Dagotto, T. Hotta, and A. Moreo, *Phys. Rep.* **344** (2001) 1.
  - [24] V.N. Smolyaninova, A. Biswas, X. Zhang, K.H. Kim, B.G. Kim, S-W. Cheong, and R.L. Green, *Phys. Rev. B* **62** (2000) R6093.
  - [25] M. Roy, J.F. Mitchell, and P. Schiffer, *J. Appl. Phys.* **87** (2000) 5831.
  - [26] R.S. Freitas, L. Ghivelder, P. Levy, and F. Parisi, *Phys. Rev. B* **65** (2002) 104403.
  - [27] W. Tong, Y. Tang, X. Liu, and Y. Zhang, *Phys. Rev. B* **68** (2003) 134435.

FIG. 1: Reflection spectra of  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$  as a function of temperature during cooling (left panel) and heating (right panel) cycles. The vertical scale corresponds to the lowest spectrum in each panel, and the other spectra are consequently shifted by 0.1 for clarity. Arrows mark the position of phonon modes, which appear in the spectra at low temperatures (see the text for details).

FIG. 2: Temperature dependent conductivity of  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$ , as obtained from the reflection in a cooling cycle. Points are experimental data, dotted lines represent Drude oscillator and high-frequency conductivity component, extrapolated to lower energies (see text for details). Solid curves, along with the two mentioned terms, include contribution of optical phonons. Note that the extrapolation of high frequency "background" crosses zero line in the two lower panels, indicating the opening of a gap.

FIG. 3: The charge density waves gap magnitude  $2\Delta$  as a function of temperature. Line is a guide to the eye.

FIG. 4: Experimental conductivity spectra of  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$  (points) as a function of temperature in a cooling cycle and their fit (solid lines) with Lorentzian oscillators, representing phonons and Drude component (dashed lines). The upper panel shows room temperature conductivity spectrum of the parent  $\text{LaMnO}_3$  compound, where a large number of relatively narrow phonon lines is observed.

FIG. 5: Temperature dependence of the integrated low-frequency conductivity (b), line intensity (a) and peak position (c,d) for several phonon modes of  $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$ . Solid lines in (c) and (d) show the temperature dependent position expected for a standard anharmonic phonon decay, while dotted lines in (a,b) are guides to the eye.

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